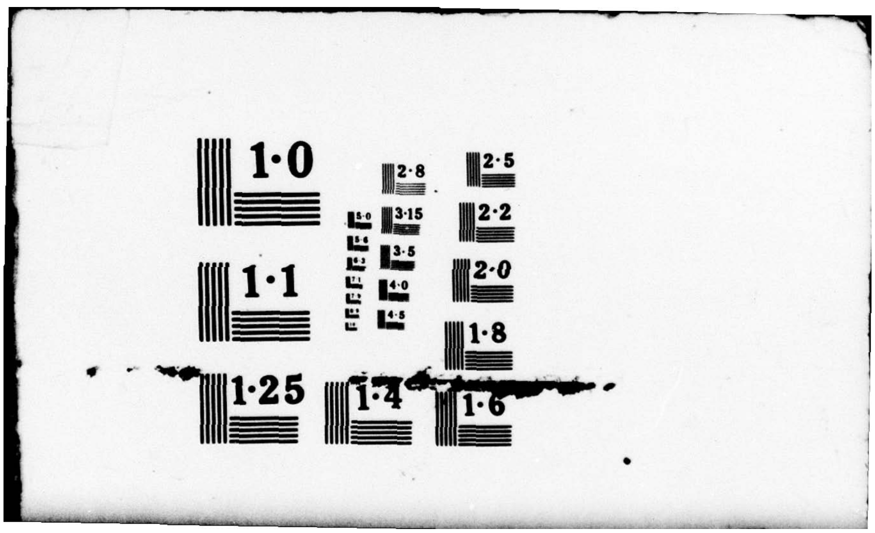
AD-A067 748 UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT O--ETC F/G 7/2
QUENCHING OF EMISSION AND OF PHOTOCHEMISTRY FOR AQUEOUS RH(NH3)--ETC(U)
APR 79 A W ADAMSON, R FUKUDA, M LARSON N00014-76-C-0548

UNCLASSIFIED TR-8 NL

1 OF 1
ADA
067748

END
DATE
FILMED
6-79
DDC


1·0
2·8
2·5
3·15
2·2
3·5
2·0
1·1
4·0
4·5
1·8
1·25
1·4
1·6

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LEVEL II

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

(12)

1. REPORT NUMBER 8 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (9)
4. TITLE (and Subtitle) (6) "Quenching of Emission and of Photochemistry for Aqueous $Rh(NH_3)_5Cl^{2+}$"		5. TYPE OF REPORT & PERIOD COVERED Technical Report No. 8, 1979
		6. PERFORMING ORG. REPORT NUMBER (15)
7. AUTHOR(s) (10) Arthur W. Adamson, Robert Fukuda, Marina Larson, Helmut Macke and Jean Pierre Puaux		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0548
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California Department of Chemistry Los Angeles, California 90007		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-609
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research (Code 472) Arlington, Va. 22217		(11) 12. REPORT DATE Apr 1979
		13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 13p.		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

(14) TR-8

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Rhodium complex
Rhodium Chloropentaammine
Emission
Emission Quenching
Photochemistry
Quenching
Hydroxide Quenching
Carbonate Quenching

PLUS OR MINUS KCAL/MOLE

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Aqueous $Rh(NH_3)_5Cl^{2+}$ shows emission and excited state absorption, ESA, decaying with the same lifetime. The temperature dependence of emission and of ESA, attributed to the first triplet thexi state, corresponds to an apparent activation energy of 5.4 ± 0.3 kcal $mole^{-1}$. The emission is quenched by OH^-, CO_3^{2-}, and CN^-, the respective bimolecular quenching rate constants for the first being 2.1×10^{10} M^{-1} sec^{-1} and 8.3×10 $M^{-1} sec^{-1}$ at 4°C. The photochemistry, predominantly chloride aquation, is also quenched. In the case of OH^-, results indicate that 85-90% of the photoreaction is quenched on complete emission

over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

LB

361555

79 04 19 079

20. Abstract (continued from previous page)

quenching. In the case of CO_3^{2-}, quenching is accompanied by some prompt anation. Less basic ions, acetate, formate, oxalate, and the species present in pH 9.2 borate solution, do not quench the emission. The quenching mechanism for OH^-, CO_3^{2-}, and CN^- is suggested to be one of proton transfer, the counter base so produced being substitution labile and able to undergo some anation during the quenching encounter.

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0548

TECHNICAL REPORT NO. 8

Quenching of Emission and of Photochemistry for Aqueous $Rh(NH_3)_5Cl^{2+}$

by

Arthur W. Adamson, Robert Fukuda, Marina Larson, Helmut Macke and Jean Pierre Puaux

Prepared for Publication in the

Journal of the American Chemical Society

Department of Chemistry
University of Southern California
Los Angeles, California 90007

April, 1979

Quenching of Emission and of Photochemistry for Aqueous $Rh(NH_3)_5Cl^{2+}$

Sir:

Both ordinary and sensitized photochemistry have been reported for various Rh(III) ammine complexes, from several laboratories.[1,2] The reactivity has been attributed to the lowest triplet thexi state, $T_1°$.[1a] Low temperature emission, also assigned to $T_1°$, has been known for some-time,[3] but has only recently been observed in room temperature, aqueous solution for $Rh(NH_3)_5X^{n+}$, for X = NH_3, ND_3, Cl, Br[4], and for X = Cl, Br, and H_2O.[5,6] In the case of $Rh(NH_3)_5Cl^{2+}$, the room temperature emission spectrum shows a maximum at 640 nm,[5] and generally resembles the low temperature spectrum.[7] There is also a transient absorption, with a maximum at 500 nm, ϵ_{max} > 100 $M^{-1}Cm^{-1}$, and assigned to $T_1°$ since the decay time is the same as that of emission.[5]

The ability to observe emission and excited state absorption (ESA) under photochemical conditions should provide leverage for excited state studies, much as has been possible for Cr(III) complexes.[2,8] We have been examining the possiblilty, and report here some results for aqueous $Rh(NH_3)_5Cl^{2+}$. Figure 1 shows the temperature dependence of the (presumed) $T_1°$ lifetime, $\tau°$, as obtained from emission and ESA.[9] The two sets of data lie on the same Arrhenius plot, of slope corresponding to 5.4 ± 0.3 kcal $mole^{-1}$ apparent activation energy. The interpolated $\tau°$ value for 25°C, 14.8 nsec, agrees well with the reported value of 14.2 nsec;[4] our value at 4°C, of importance below, is 30.1 ± 0.7 nsec.

We find that the emission is quenched by OH^- and by CO_3^{2-} ions (that the behavior is the same for ESA was checked in the case of OH^-), and the Stern-Volmer type plots for 4°C are shown in Figure 2. Carbonate ion has not previously been reported as a quencher for an excited state of a coordination compound.[12] The slopes of the two Stern-Volmer plots yield bimolecular quenching rate constants, k_q, of 2.1×10^{10} and 8.3×10^{9} $M^{-1}sec^{-1}$ for OH^- and CO_3^{2-}, respectively. These k_q values correspond to about the diffusion encounter rates expected for the two quenchers. That the quenching is due to CO_3^{2-} rather than to HCO_3^-, is indicated by the agreement of the dark circle point of Figure 2, for $[CO_3^{2-}] = 7.5 \times 10^{-4}$ M, $[HCO_3^-] = 9.0 \times 10^{-3}$ M, with the adjacent open circle point, for $[CO_3^{2-} = [HCO_3^-] = 8.0 \times 10^{-4}$ M.

An important aspect that may now be tested is the degree to which emission quenching leads to reduction in photochemical quantum yield. The 25°C yields for chloride and for ammonia photoaquation are reported to be 0.16 and $< 10^{-3}$, respectively.[1a] Our procedure, in testing for OH^- quenching, was to carry out paired irradiations, one in pH 2 perchloric acid solution, and one at the desired OH^- concentration, and to compare the spectrophotometrically determined degrees of photolysis.[13] Three results for $\phi°/\phi$, the ratio of quantum yield for acid vs. alkaline solution, are shown in Figure 2, the estimated error in each being about ± 10%.[13] A fourth result, for 0.013 M OH^-, gave $\phi°/\phi = 4.4$. Photolysis quenching was also observed qualitatively, in the case of CO_3^{2-} solutions, but with indication of complexity in that some prompt formation of $Rh(NH_3)_5(CO_3)^+$ occurred.

It has been suggested, from deuteration effects on emission lifetime and photochemical quantum yield, that the photoaquation and emission are competitive.[4] Our results tend to confirm this conclusion in that emission quenching is indeed accompanied by quenching of photochemistry. Our $\phi°/\phi$ values lie below the emission quenching line, however, and, in the cases of the two higher OH^- concentrations, to an extent well exceeding experimental uncertainty. (The point at 0.013 M OH^-, not shown in Figure 2, $\phi°/\phi = 4.4$, is to be compared with the value of 9.3 predicted by extrapolation of the

$\tau°/\tau$ plot.) The data are fit, however, by the dashed line in the figure, calculated for 13% unquenchable photoreaction. This could be due either to reaction from an excited state not populated via $T_1°$, or to some anation during a quenching encounter.

Results of tests for other quenchers are that we detect no emission quenching by acetate, formate, or oxalate ions, or by the species present in 0.05 f borate at pH 9.2. Cyanide ion is a weak quencher, with 25% lifetime quenching in 0.05 f cyanide at pH 9.3. The three quenching species, OH^-, CO_3^{2-}, and CN^-, have the common property of being good proton acceptors; it may be that there is a common quenching mechanism of proton transfer from $T_1°$ to base, B^-, during a quenching encounter. The immediate product, $[Rh(NH_3)_4(NH_2)Cl\cdot HB]^+$, should be substitution labile, and might in part convert to $Rh(NH_3)_5B^{n+}$. Such behavior would account for our results with OH^- and for the component of prompt anation in the case of CO_3^{2-}.

Acknowledgements. This investigation has been supported by the U.S. National Science Foundation, and the U.S. Office of Naval Research. One of us (HM) acknowledges a fellowship from the Swiss National Science Foundation.

References and Notes

(1) (a) T. L. Kelly and J. F. Endicott, J. Phys. Chem., 76, 1937(1972); J. F. Endicott and G. J. Ferraudi, J. Phys. Chem., 80, 849 (1976).
(b) M. M. Muir and W. L. Huang, Inorg. Chem., 12, 1831 (1973).
(c) C. Kutal and A. W. Adamson, Inorg. Chem., 12, 1454 (1973).
(d) P. C. Ford and J. D. Petersen, Inorg. Chem., 14, 1404 (1975).
(See also references cited in the above.)

(2) (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, 1970. (b) A. W. Adamson and P. D. Fleischauer, eds., "Concepts of Inorganic Photochemistry," Wiley, New York, 1975.

(3) T. R. Thomas, R. J. Watts, and G. A. Crosby, J. Chem. Phys., 59, 2123 (1973), and references therein.

(4) M. A. Bergkamp, R. J. Watts, P. C. Ford, J. Brannon, and D. Magde, Chem. Phys. Lettr., 59, 125 (1978).

(5) A. W. Adamson, Pure and Applied Chem., 51, 313 (1979). Note: the uncorrected emission spectrum using a photomultiplier rather than the vidicon detector has a maximum at 670 nm.

(6) Unpublished work in this laboratory.

(7) T. R. Thomas and G. A. Crosby, J. Molec. Spectr., 38, 118 (1971).

(8) (a) A. W. Adamson, R. T. Walters, R. Fukuda, and A. R. Gutierrez, J. Amer. Chem. Soc., 100, 5241 (1978). (b) A. R. Gutierrez and A. W. Adamson, J. Phys. Chem., 82, 902 (1978). (c) R. T. Walters and A. W. Adamson, Acta. Chem. Scand., in press.

(9) $[Rh(NH_3)_5Cl]Cl_2$ was obtained from Alpha Inorganics; $[Rh(NH_3)_5(H_2O)](ClO_3)_3$ and $[Rh(NH_3)_5(CO_3)](ClO_4)$ were prepared according to literature protocols.[10,11] The pulsed Nd glass laser and associated equipment used is essentially that described preivously;[8] exciting pulses were at 353 nm and of 5 nsec and 20 nsec half-width in the cases of the emission and ESA measurements, respectively. Emission intensities were followed at 670 nm, and ESA's were monitored at 485 nm.

(10) G. W. Bushnell, G. C. Lalor, and E. A. Moelwyn-Hughes, J. Chem. Soc. (A), 719 (1966).

(11) D. A. Palmer and G. M. Harris, Inorg. Chem., 13, 965 (1974).

(12) As a cautionary note, CO_3^{2-} may easily be present as adventitious impurity in basic solutions; its quenching ability was discovered as a result of investigating the source of irreproducibilities in preliminary

experiments. In subsequent ones, care was taken to use A.R. or "super pure" grade sodium hydroxide, which was water washed and immediately made up to a stock solution. Dilutions were made with care to minimize absorption of atmospheric CO_2, and irradiations, in sealed cells. Hydroxide ion concentration was calculated from the measured pH at 25°C. The carbonate solutions were equiformal in $NaHCO_3$ and Na_2CO_3, and had a pH of 10.08.

(13) It was first verified that no different photochemistry occurred in the alkaline solutions. The solution was acidified after photolysis, and the spectrum found to correspond to that for a stage in the acid photolysis. Also, since the absorption spectra for $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5(H_2O)^{3+}$, and $Rh(NH_3)_5(OH)^{2+}$ are known,[14,15] independent (and agreeing) determinations of the course of photolysis in either acid or alkaline solution could be made by suitable plotting (see Ref. 16) of optical density changes at various wavelengths. Photolyses of the 0.003 M $Rh(NH_3)_5Cl^{2+}$ were 10% to 20% reaction and some pH decrease of the OH^- solutions occurred; the points in Figure 2 are for the average OH^- concentration during the photolysis.

(14) P. E. Hoggard and H. Schmidke, Ber. Bun. Ges., Physik. Chemie, 59, 2123 (1973).

(15) C. K. Jørgensen, Acta Chem. Scand., 10, 500 (1956).

(16) P. S. Sheridan and A. W. Adamson, J. Amer. Chem. Soc., 96, 3032 (1974).

Arthur W. Adamson,* Robert Fukuda, Marina Larson, Helmut Mäcke, and Jean Pierre Puaux.

Department of Chemistry, University of Southern California,

Los Angeles, California 90007

Legends for the figures.

Figure 1. Temperature dependence of emission and ESA lifetimes for aqueous $Rh(NH_3)_5Cl^{2+}$. O Emission; Δ ESA; ● datum from Ref. 4. Numbers in parentheses give the number of separate experiments.

Figure 2. Stern-Volmer plot of OH^- and CO_3^{2-} quenching of aqueous $Rh(NH_3)_5Cl^{2+}$ at 4°C. Δ OH^- quenching of emission. ▲ OH^- quenching of photolysis. O CO_3^{2-} quenching of emission. ● Test of effect of $[HCO_3^-]$, see text. Numbers in parentheses give the number of separate experiments.

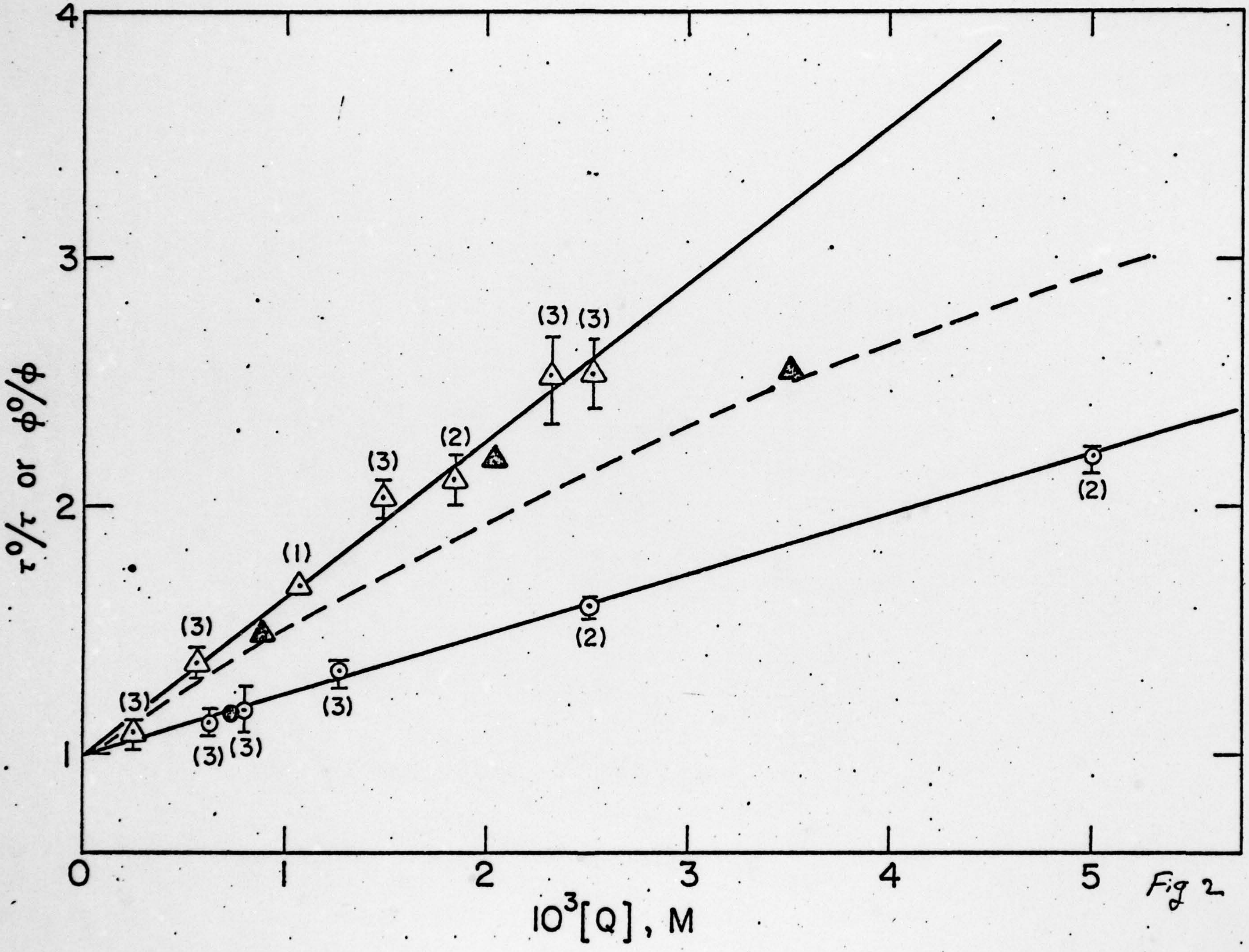


Fig 2

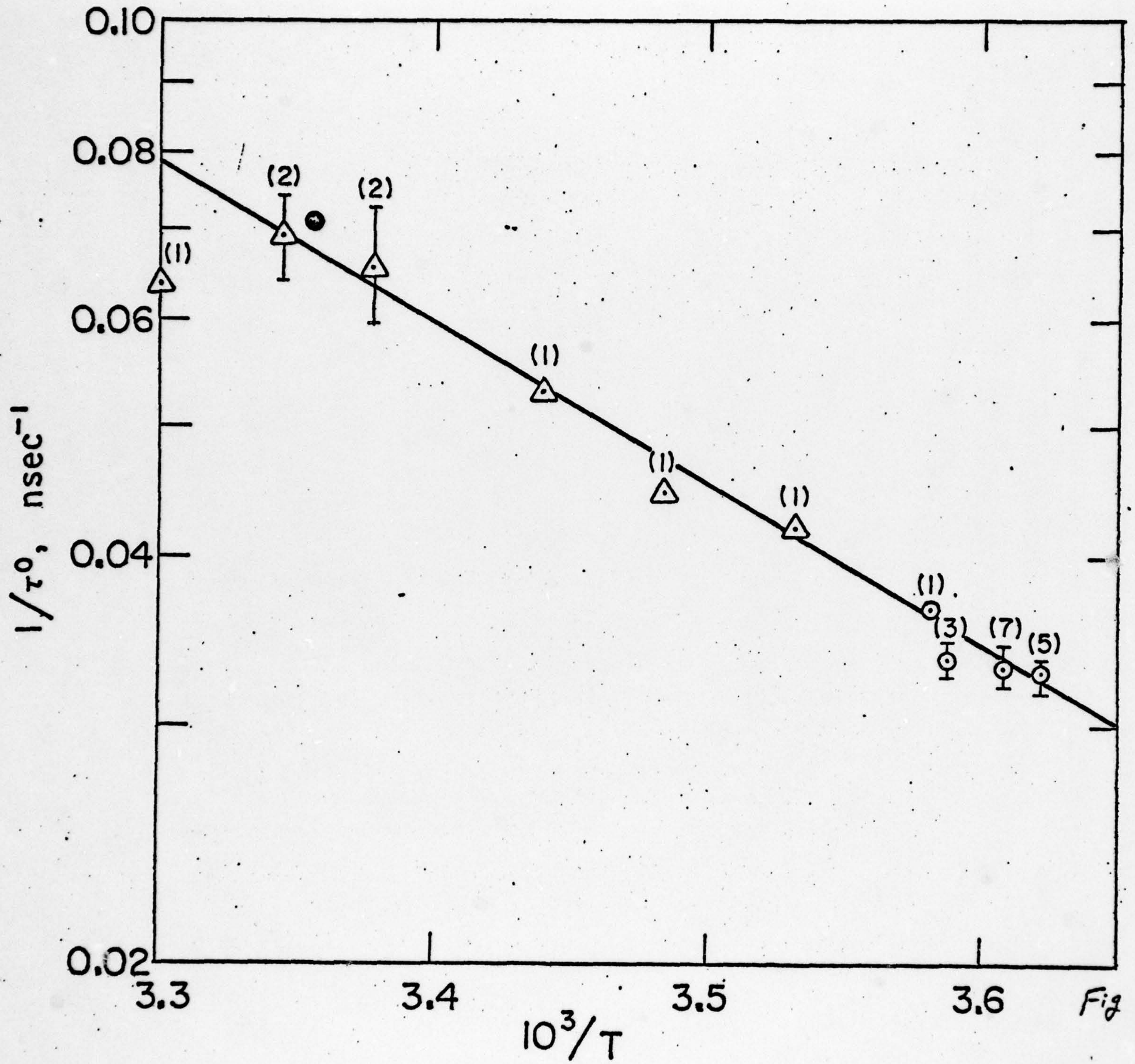


Fig 1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
~~Office of Naval Research~~ ~~Arlington, Virginia 22217~~ ~~Attn: Code 102IP 1~~	~~6~~
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1 ✓
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1

	No. Copies
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. M. A. El-Sayed University of California Department of Chemistry Los Angeles, California 90024	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	1
Dr. E. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1
Dr. M. H. Chisholm Princeton University Department of Chemistry Princeton, New Jersey 08540	1
Dr. J. R. MacDonald Naval Research Laboratory Chemistry Division Code 6110 Washington, D.C. 20375	1

	No. Copies
Dr. G. B. Schuster University of Illinois Chemistry Department Urbana, Illinois 61801	1
Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah 84112	1
~~Dr. A. Adamson~~ ~~University of Southern California~~ ~~Department of Chemistry~~ ~~Los Angeles, California 90007~~	~~1~~
Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
Dr. M. Rauhut American Cyanamid Company Chemical Research Division Bound Brook, New Jersey 08805	1